Chapter 56 – SANS FROM POLYMERIC MATERIALS

Materials Science is one of the major SANS research areas. A host of Materials Science projects are performed using the SANS technique. Here, a couple of projects in which this author was involved are described. Focus is on macromolecular orientation in polymeric materials associated with various types of deformation and processing. Macromolecular orientation affects the mechanical properties of polymeric materials.

1. MATERIALS AND METHOD

The projects described here use partially deuterated polystyrene to monitor macromolecular chain deformations associated with specific sample treatments. Deuterated atactic polystyrene (dPS) of M_w = 338,000 g/mol and M_n = 239,000 g/mol and hydrogenated (normal) polystyrene (hPS) of comparable molecular weight have been synthesized and characterized by GPC. A 5 % dPS weight fraction was mixed to hPS in solution. The homogeneous mixture was then dried. Various partially deuterated PS plates of uniform thickness were produced using the melt-pressing method.

The SANS technique was used to monitor macromolecular chain orientation associated with various sample treatments such as hot-stretching, injection molding and shear band formation. The SANS instrument used (University of Missouri Research Reactor) uses a neutron wavelength of 4.75 Å. This wavelength is obtained using a pyrolytic graphite monochromator with a 90º diffraction angle. SANS data analysis consisted in a standard sector averaging method as well as in the elliptical averaging method which results in radii of gyration parallel and perpendicular to the orientation direction. The birefringence method was also used in some cases in order to compare chain orientations. The birefringence method averages over inter-chain contributions and can be measured over small spot sizes whereas the SANS technique is more sensitive to single-chain orientation. SANS sample thickness varied between 1 and 2 mm and the spot size diameter was 1 cm. Single-chain scattering was represented by the familiar Debye function for Gaussian polymer coils.

2. MACROMOLECULAR ORIENTATION WITH HOT STRETCHING

The 5 % dPS/hPS homogeneous polymer mixture was compression molded into bars that were hot stretched in an Instron machine for stretching ratios from 1 to 4 at a temperature of 110 ºC; i.e., slightly above the softening glass-rubber transition temperature T_g for PS. Upon reaching the desired External Draw Ratio (EDR) the samples were quenched in water at 23 ºC.

SANS measurements were made from the hot stretched PS samples after and before hot stretching (Hammouda et al, 1986). Radii of gyration R_{gy} and R_{gx} along and perpendicular to the stretch direction after hot stretching and R_{g0} before hot stretching

were obtained. Iso-intensity contour maps displayed elliptical asymmetry. The elliptical eccentricity ε is defined as the ratio $\varepsilon = R_{gx}/R_{gy}$. The Molecular Draw Ration (MDR) is defined as $MDR = R_{gy}/R_{g0}$. Assuming that the molecular volume is conserved during deformation and that the x and z directions are equivalent, the MDR would also be given by $\sqrt{MDR} = R_{gx}/R_{g0}$.
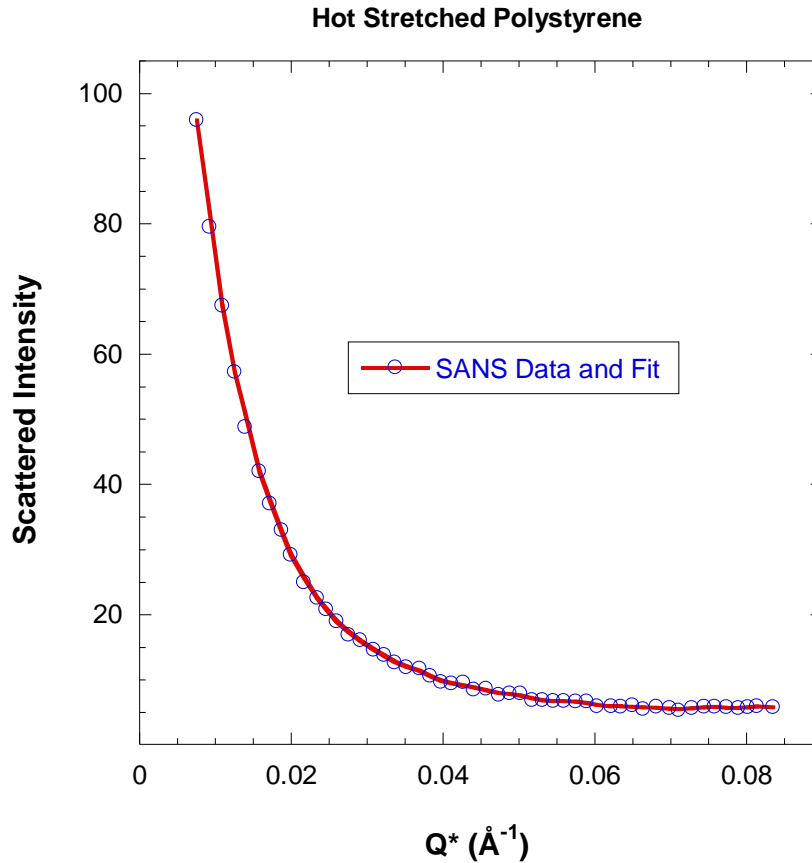

Figure 1: Typical SANS data from a hot stretched sample along the stretching direction and fit to the Debye function.

A table summarizes the hot stretching conditions that produced the five samples and the radii of gyration results obtained from SANS measurements at ambient temperature. The birefringence measurements have also been included.

Table 1: Hot stretched samples and chain orientation results obtained from SANS and birefringence measurements

Sample	Load (lbs)	Stretch Rate (inch/min)	Temp (°C)	EDR	Eccent. ε	R_{gy} (Å)	R_{gx} (Å)	MDR	Birefring. $*10^3$
CDS1	12.8	10	110	2.0	.45	249	112	1.70	5.74
CDS2	15.1	10	110	1.5	.75	170	127	1.21	1.78
CDS3	11	10	110	2.75	.33	293	97	2.09	8.80

CDS4	10	5	110	4	.30	330	99	2.23	10.02
CDS5	--	10	110	1.75	.54	214	116	1.51	4.21

A plot of the MDR vs EDR shows that chain deformations become nonlinear (i.e., non-affine) for large EDR values. Note that the trends obtained from SANS and birefringence measurements are similar.
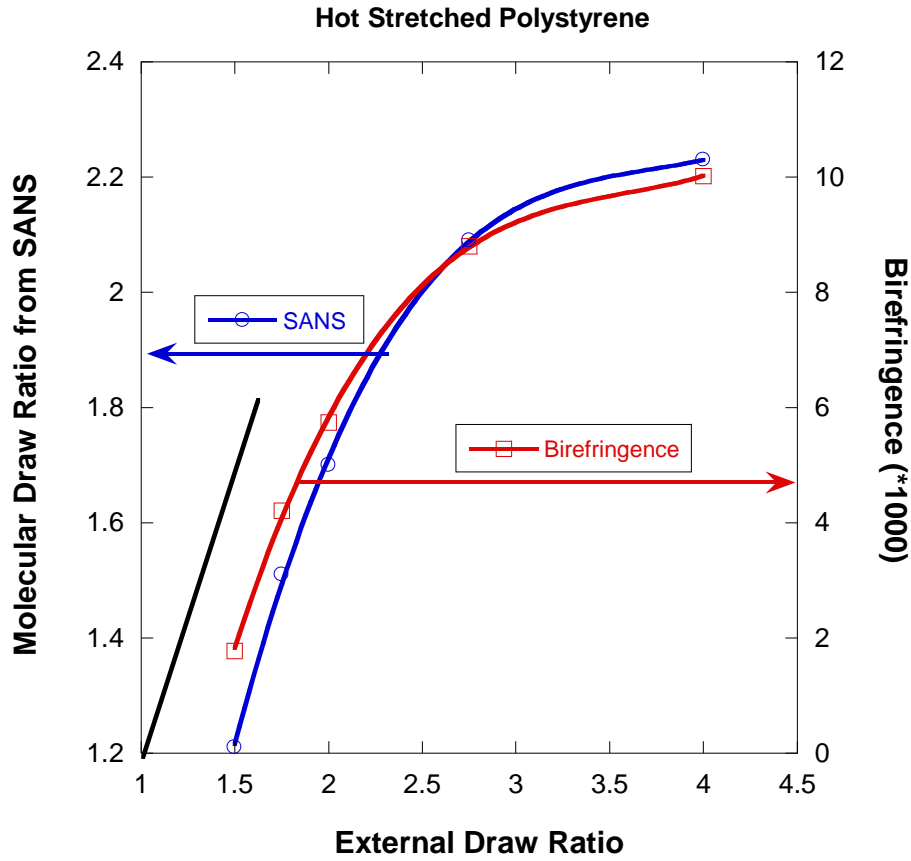

Hot Stretched Polystyrene

Figure 2: Plot of the MDR for varying EDR. Results from SANS and birefringence measurements are included. The line with a slope of 1 is also shown.

The SANS technique has been used more recently to investigate residual orientation in injection molded polymer samples (Healy et al, 2006).

3. HOT STRETCHING REVISITED

Similar SANS measurements were performed on another series of partially deuterated hot stretched polystyrene bars (Schroeder, 1991). The deuteration level was increased to 20 % for increased sensitivity. The MDR were obtained and plotted with increasing EDR. The SANS results were compared to rubber elasticity models. The simplest model assumes an affine deformation whereby $R_{gy} = R_{g0} * EDR$ and $R_{gx} = R_{g0} / \sqrt{EDR}$

where R_{gy}, R_{gx} and R_{g0} are the radii of gyration parallel, perpendicular and before stretching respectively. The prediction for the direction perpendicular to stretching falls on top of the data while the prediction parallel to the stretching direction is far from the data points. Polynomial fit to the data parallel to the stretch direction yielded a good fit to a second order polynomial.

Hot Stretched Polystyrene

Parallel Data Fit	
$Y = M0 + M1*x + ... M8*x^8 + M9*x^9$	
M0	0.059124
M1	1.0452
M2	-0.10817
R	0.99998

Legend:
— Parallel Data and Fit
— Affine Model Prediction
— Perpendicular Data and Fit

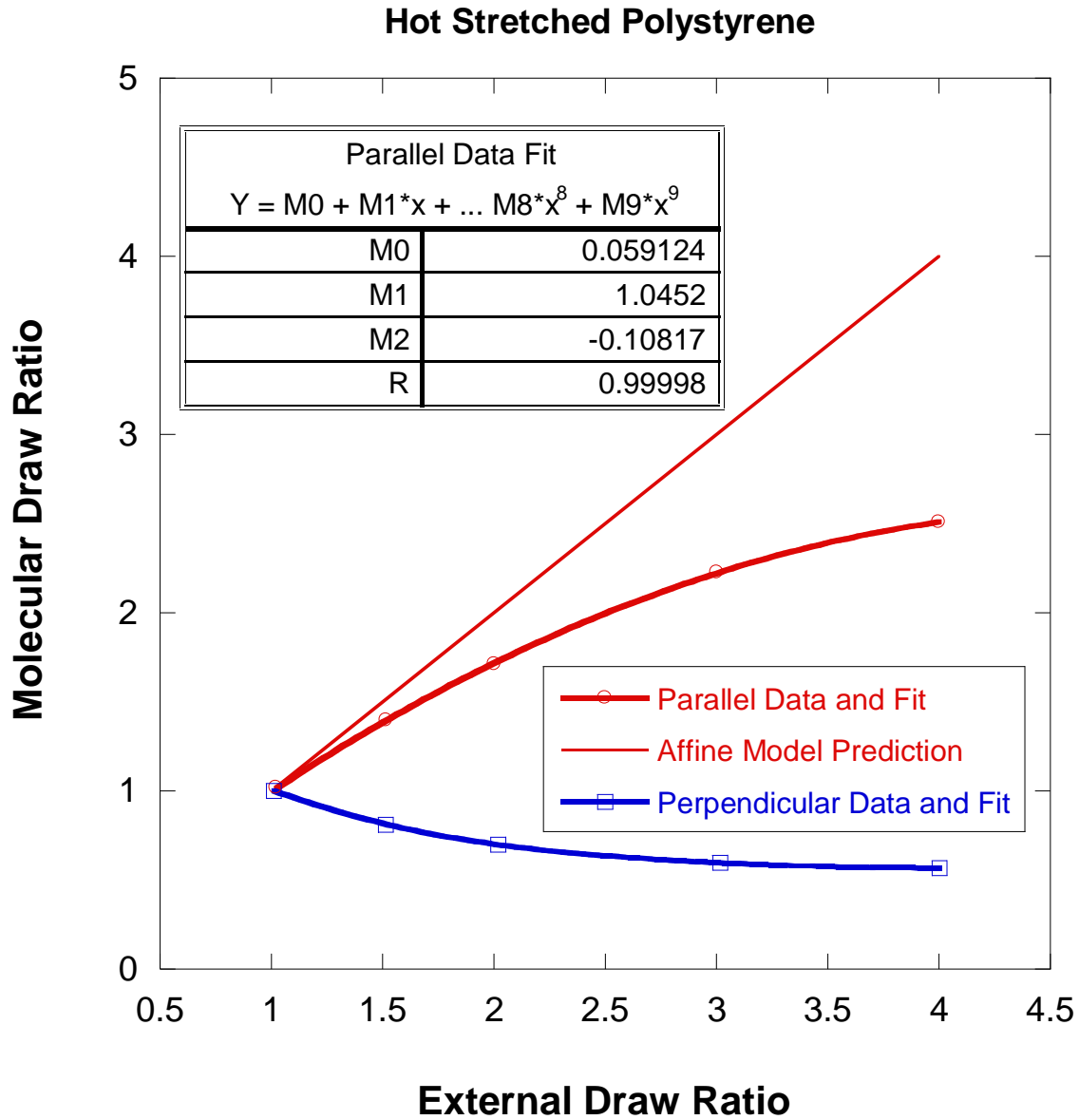(X axis: External Draw Ratio, 0.5 to 4.5; Y axis: Molecular Draw Ratio, 0 to 5)

Figure 3: Variation of the MDR with EDR along with predictions of a rubber elasticity model.

More precise elliptical fitting of the iso-intensity contour maps showed that the eccentricity depends on the scattering variable Q, and therefore on the length scale in direct space.

4. MACROMOLECULAR ORIENTATION WITH INJECTION MOLDING

Injection molding is the most widely used method for polymer processing. It is characterized by high repetition rates, low cost and high precision. During the injection, packing and cooling stages of the molding process, flow and thermal stresses develop resulting in preferential orientation of the polymer chains. Macromolecular orientation associated with injection molding was investigated using the SANS technique on the same 5 % dPS/hPS polystyrene mixture (Hammouda et al, 1986). 5 cm diameter disks and 2 cm wide by 15 cm long bars were injection molded using specific conditions.

Table 2: Injection molding conditions

	Cold Conditions	Hot Conditions
Melt Temperature	167 ºC	229 ºC
Pressure	3700 psi	2500 psi
Injection Time	8 s	8 s
Cooling Time	30 s	30 s
Band Temperature	176 ºC	246 ºC
Mold Temperature	24 ºC	65 ºC

Injection molded bars and disks were 3 mm thick. This thickness was chosen in order to be able to mill down a few spots in order to observe chain orientation close to the skin surface or deep inside the bulk. The milled down spots had an optimal thickness of 1.5 mm appropriate for SANS.
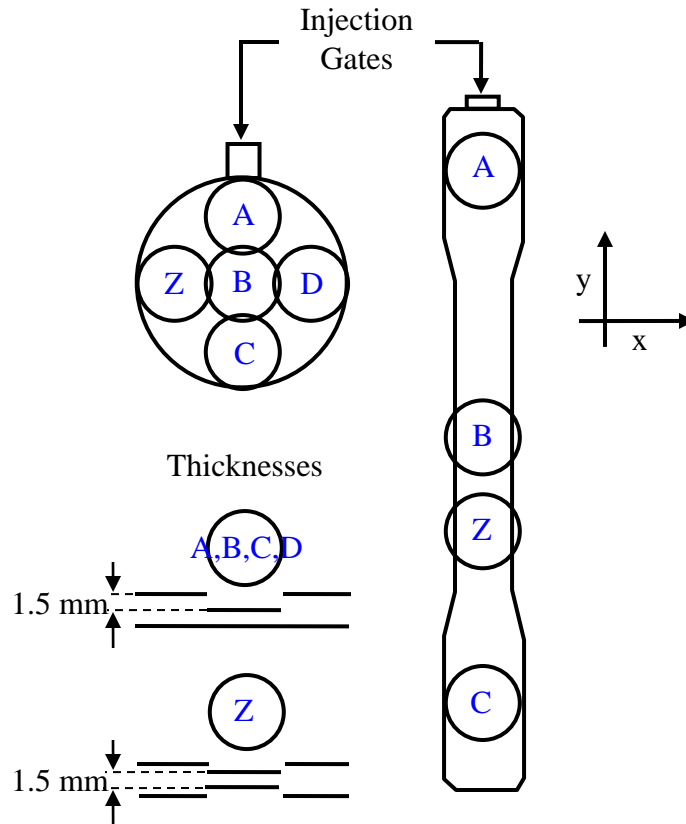
Figure 4: Injection molded disk and bar.

SANS measurements were performed and eccentricity factors (ε) and orientation angles of the iso-intensity contour maps were obtained. Representative results are included here.

Table 3: Eccentricity and orientation angle for one of the injection molded samples (cold molded disk).

	Eccentricity	Orientation Angle (degrees)
Spot A	.63	5
Spot B	.77	9
Spot C	.87	24
Spot D	.79	38
Spot Z	.92	40

Analysis of the SANS results yielded the following conclusions: there is more macromolecular chain orientation close the injection gate than away from it, close to the sample surface than deep inside, in open parts of the sample than in corners. Moreover, the "cold" condition injection molding showed more orientation than the "hot" condition.

5. MACROMOLECULAR ORIENTATION IN SHEAR BAND DEFORMATIONS

Polymeric materials have two main modes of deformation: the elastic and the plastic modes. The plastic mode is of interest since it involves irreversible mechanisms of deformation. Shear bands form in notched and compressed samples. Birefringence has been the main technique to investigate macromolecular chain orientation within shear bands. It was found that shear band packet propagates at 38° from the compression axis and that there is formation of a diffuse shear zone which propagates ahead of the shear band at 45°.

In order to investigate chain orientation within shear bands using the SANS technique, a 2 mm thick plaque of 5 % dPS/hPS mixed polystyrene was molded. Identical rectangular plates (2 cm*4 cm) were cut out, sharply notched (notch was less than 1 mm deep) and compressed in a special device (Bubeck et al, 1986). Cases corresponding to fast and slow compression were considered. After compression schemes taking of order of minutes at various temperatures, the device was locked at the target strain, cooled to ambient temperature after which SANS data were taken. A new sample was used for each case. The compression was along the y axis making the x-y plane parallel to the scattering plane.

Four holes for heater probes

Cadmium internal lining

Holes for thermocouples

Thin aluminum windows

Disk to center the device on the sample tray

Side spacers

Notched sample

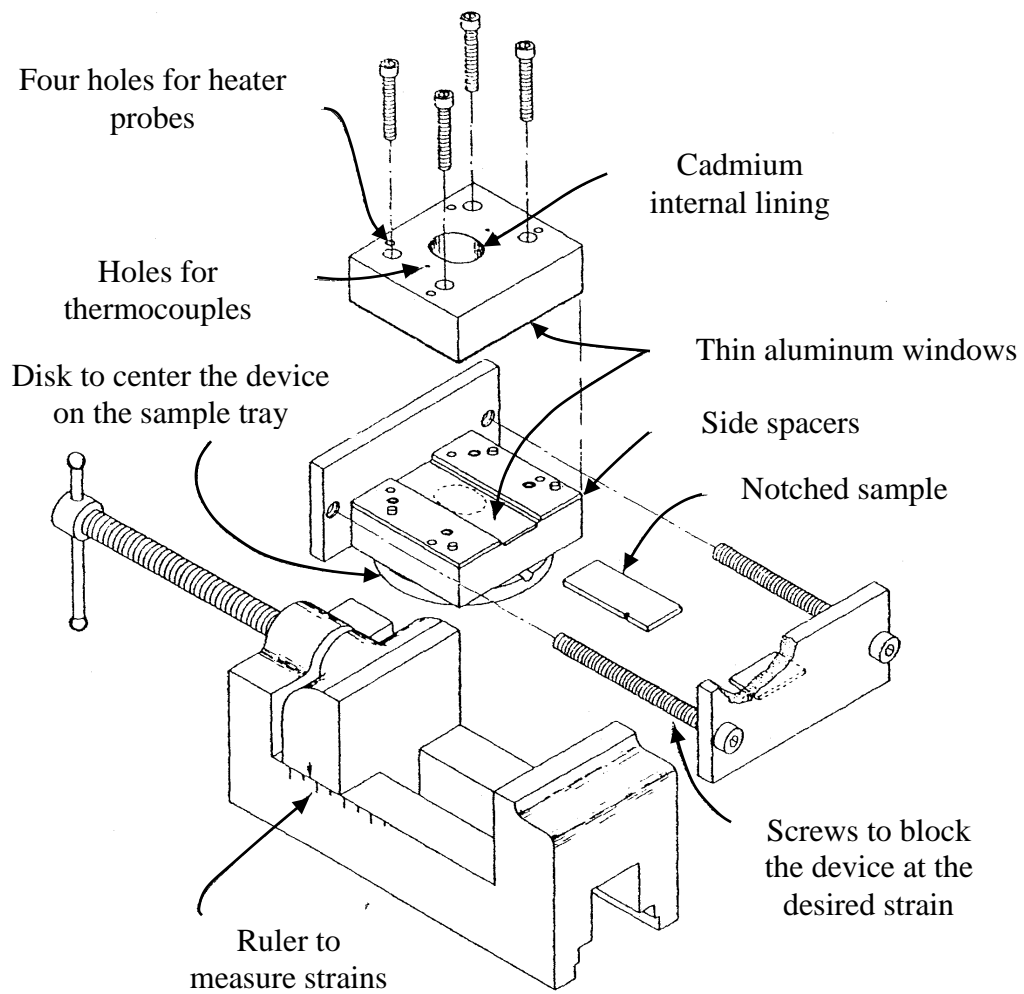Screws to block the device at the desired strain

Ruler to measure strains

Figure 5: Representation of the device used to create shear bands.
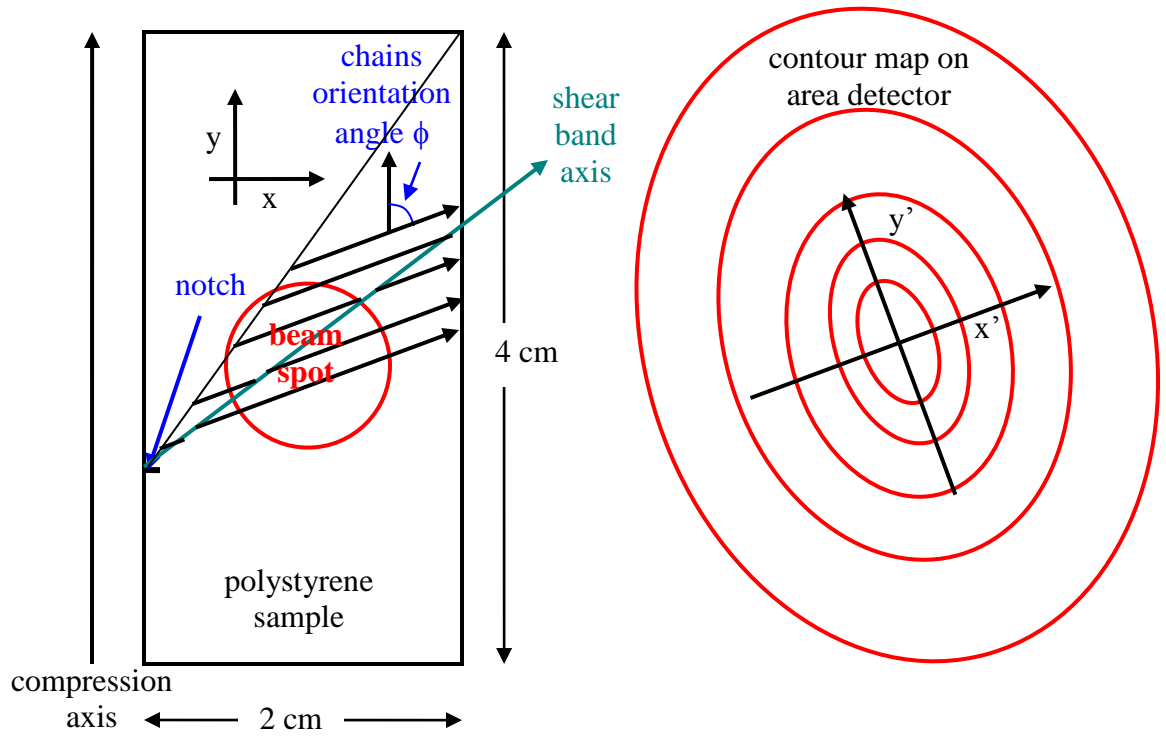
Figure 6: Representation of the sample plane (in direct space) and of the scattering plane (reciprocal space). Note that the neutron area detector is 64 cm*64 cm whereas the sample is 2 cm*4 cm.

Results of the SANS data analysis are summarized in a table. The radii of gyration parallel (y') and perpendicular (x') to the chain orientation axis were obtained using fits to the Debye functional form. An overall radius of gyration was also obtained as

$R_g = \sqrt{(R_{gy'}^2 + 2R_{gx'}^2)/3}$. The eccentricity was obtained as the ratio $\varepsilon = R_{gx'}/R_{gy'}$.

Table 4: Conditions used to create shear bands and SANS macromolecular orientation results.

Temperature (°C)	Strain (%)	Strain Rate (s⁻¹)	Eccentricity ε	Orientation Angle (degrees)	$R_{gy'}$ (Å)	$R_{gx'}$ (Å)	R_g (Å)
80	7.5	$5*10^{-3}$	.90	80	138	124	129
60	7.5	$5*10^{-3}$	.90	82	168	151	157
40	7.5	$5*10^{-3}$	.90	84	165	148	154
90	7.5	$5*10^{-4}$	.82	79	148	131	137
70	7.5	$5*10^{-4}$	.84	78	158	133	142
50	7.5	$5*10^{-4}$	.82	78	170	139	150

30	7.5	$5*10^{-4}$	.82	84	181	148	160
90	12.5	$4.6*10^{-4}$	.74	80	152	112	127
80	12.5	$4.6*10^{-4}$	.72	78	157	113	129
70	12.5	$4.6*10^{-4}$	.74	78	160	118	133
50	12.5	$4.6*10^{-4}$	.73	77	160	117	133
40	12.5	$4.6*10^{-4}$	.72	78	161	116	133
20	12.5	$4.6*10^{-4}$	.78	76	154	120	132

Some of the conclusions from the SANS results are included here. Macromolecules participating in the shear band are oriented at about 81° from the compression axis regardless of the compression conditions (temperature, strain and strain rate). This is in agreement with the birefringence measurements showing a 38°+45° = 83° orientation angle. Only glide modes of deformation of elongated coils are observed in the shear bands. Diffusion modes are not prominent in our measurement conditions. Non-affine chain deformation was observed. These are plastic modes of deformation. Saturation was observed for the high strain rate case.

REFERENCES

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J.R. Schroeder, B. Hammouda, R.A. Bubeck and J.W. Chang, "SANS from Hot Stretched Polystyrene Revisited", J. Polym. Sci., Polym. Phys. Ed. 29, 1607-1612 (1991)

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QUESTIONS

1. How to hot stretch a polymer bar? What instrument is used for that?
2. How is injection molding performed? What are the determining factors?
3. What are shear bands? How to create them?
4. Why is the Debye function adequate for the description of polymer chains in the melt?
5. Name two methods that are sensitive to macromolecular chain orientation.

ANSWERS

1. A polymer bar is hot stretched by heating slightly above the softening glass-rubber transition temperature (T_g), stretching to the desired external draw ratio and quenching in cold water. The Instron machine is used for hot stretching.

2. Injection molding is performed by melting the polymer, injecting the melt into a mold, then cooling down. Temperature, pressure and injection rate are the determining factors.

3. Shear bands are a form of plastic deformation in polymeric materials. Shear bands are obtained by notching and compressing a sample which is confined in order to avoid buckling.

4. Polymer chains follow Gaussian chain statistics in the melt state; i.e., they follow a random walk with no excluded volume.

5. Two methods that are sensitive to macromolecular chain conformation are optical birefringence and SANS. SANS is more sensitive but requires partially deuterated samples.